

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
8 March 2001 (08.03.2001)

PCT

(10) International Publication Number  
**WO 01/17041 A1**

(51) International Patent Classification<sup>7</sup>: **H01L 51/40**

(74) Agent: ROSE, Jamie, H.; Testa, Hurwitz & Thibault, LLP, High Street Tower, 125 High Street, Boston, MA 02110 (US).

(21) International Application Number: PCT/US00/24091

(22) International Filing Date: 31 August 2000 (31.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/151,715	31 August 1999 (31.08.1999)	US
60/151,716	31 August 1999 (31.08.1999)	US
09/621,000	21 July 2000 (21.07.2000)	US

(71) Applicant: E INK CORPORATION [US/US]; 733 Concord Avenue, Cambridge, MA 02138 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(72) Inventors: AMUNDSON, Karl; 56 Kirkland Street #1, Cambridge, MA 02138 (US). DRZAIC, Paul, S.; 2 Pad-dock Lane, Lexington, MA 02421 (US). WANG, Jianna; 5 Dolores Avenue, No. 8, Waltham, MA 02452 (US). DUTHALER, Gregg; 1243 Beacon Street, Brookline, MA 02446 (US). KAZLAS, Peter; 405 Dutton Road, Sudbury, MA 01776 (US).

(54) Title: METHOD FOR FORMING A PATTERNED SEMICONDUCTOR FILM

(57) Abstract: A process for forming a pattern in a semiconductor film is provided. The process comprises the steps of: providing a substrate; providing an organic semiconductor film adjacent the substrate; and providing a destructive agent adjacent selected portions of the organic semiconductor film, the destructive agent changing a property of selected portions of the organic semiconductor film substantially through the full thickness of the organic semiconductor film such that the property of the selected portions of the organic semiconductor film differs from the property of remaining portions of the organic semiconductor film. A method for manufacturing a transistor comprises the steps of: providing a substrate; providing a gate electrode adjacent the substrate; providing a gate dielectric adjacent the substrate and the gate electrode; providing a source electrode and a drain electrode adjacent the gate dielectric; providing a mask adjacent the gate dielectric in a pattern such that the source electrode, the drain electrode, and a portion of the gate dielectric remain exposed; and providing a semiconductor layer comprising one of an organic semiconductor and a plurality of inorganic colloidal particles, adjacent the source electrode, the drain electrode, the portion of the gate dielectric and the mask, thereby forming the transistor, the semiconductor layer having a thickness less than a thickness of the mask.

**BEST AVAILABLE COPY**

WO 01/17041 A1



## METHOD FOR FORMING A PATTERNED SEMICONDUCTOR FILM

Related Applications

This application is a continuation in part of U.S.S.N. 09/621,000 filed on July 21, 2000 which is a continuation in part of U.S.S.N. 09/289,036 filed on April 9, 1999 and which claimed benefit of provisional applications U.S.S.N. 60/144,943 filed on July 21, 1999 and U.S.S.N. 60/147,989 filed on August 10, 1999, and claims benefit of provisional applications 60/151,716  
5 filed on August 31, 1999 and U.S.S.N. 60/151,715 filed on August 31, 1999. The entire contents of all the aforementioned applications are incorporated herein by reference.

Technical Field

The invention relates generally to manufacturing of semiconductor devices and more particularly to the patterning of semiconductor films in the manufacture of arrays of transistors  
10 for use in display devices.

Background of the Invention

The fabrication of all-printed backplanes on polymeric substrates through use of solvent-based inks offers the potential for lower cost, flexible, or large area displays. There are numerous potential applications for such displays, such as rolled displays, affordable large area displays,  
15 displays incorporated into fabrics, and as a paper substitute. Unfortunately, many problems remain in the development of thin-film transistor ("TFT") arrays used for addressing in such displays.

Organic semiconductor materials or dispersions of inorganic semiconducting particles lend themselves to relatively simple and inexpensive deposition methods. Possible methods  
20 include thermal evaporation in a vacuum chamber or wet processing such as spin coating using an appropriate solvent or by other coating techniques known to yield thin films.

- 2 -

Some deposition techniques have the advantage of forming thin films of organic semiconductor that have desirable properties such as a high field effect mobility for the dominant charge carrier in the film. For example, it is known that vacuum deposition of oligothiophenes such as  $\alpha$ -sexithiophene, or  $\alpha,\omega$ -dihexyl quaterthiophene under proper processing conditions, gives films that exhibit a high field effect mobility.

Unfortunately, wet deposition processes do not readily permit patterning of the film because the wet material is generally distributed over the entire substrate. Vacuum deposition can be done in a patterned way using, for example, of a contact mask. Fine details, however, are difficult to pattern because of resolution limits of contact masks for vacuum deposition. Well established silicon-based device patterning methods, such as photolithography, are relatively complex and expensive. Such patterning methods conflict with the desire to manufacture relatively inexpensive arrays of transistors.

What are needed are relatively simple, low cost manufacturing methods for production of patterned semiconductor films to help realize the advantages of large array and flexible displays.

#### Summary of the Invention

The present invention provides a method to pattern semiconductor layers, in particular for use in the manufacture of lower cost, larger area transistor arrays. Use of lower cost deposition methods, such as printing techniques, enables realization of the benefits of large area displays, in particular displays employing an encapsulated electrophoretic display medium.

One embodiment of a process for forming a patterned semiconductor film comprises providing a substrate and an organic semiconductor film adjacent to the substrate. A destructive agent is deposited adjacent to selected portions of the organic semiconductor film where the destructive agent is chosen to change a property of selected portions of the organic semiconductor film substantially through the full thickness of the organic semiconductor film.

- 3 -

The destructive agent can comprise a solvent that serves to dissolve neighboring portions of the organic semiconductor layer. Other materials can be employed to cause gross damage to portions of the semiconductor layer, such as an oxidizer to cause oxidation of the neighboring portions of the semiconductor layer.

50 Alternatively, a portion of the destructive agent can diffuse into neighboring portions of the organic semiconductor film and impair the electrical properties of those portions of the film. Damaged portions of the organic semiconductor film preferably have reduced conductivity and may act as an insulator. These portions provide electrical isolation between neighboring transistors in an array.

55 The destructive agent can further comprise a gelling agent. The gelling agent assists, for example, in deposition of the destructive agent via printing methods.

In another embodiment, a method for manufacturing a transistor comprises the provision of a substrate and a gate electrode adjacent to the substrate. A gate dielectric is deposited adjacent to the substrate and the gate electrode. Source and drain electrodes are deposited  
60 adjacent to the gate dielectric. A mask is deposited adjacent to the gate dielectric in a pattern such that the source electrode, the drain electrode, and a portion of the gate dielectric remain exposed and a semiconductor layer comprising one of an organic semiconductor and a plurality of inorganic colloidal particles is deposited adjacent to the source electrode, the drain electrode, the portion of the gate dielectric and the mask, thereby forming the transistor, the semiconductor  
65 layer having a thickness less than a thickness of the mask. In some embodiments, the thickness of the semiconductor layer is 1/50 to 1/1000 of the thickness of the mask.

In some bottom contact transistor embodiments, the mask need not be removed since it can disrupt the continuity of the semiconductor layer between neighboring transistors. The mask further leads to an effective increase in the spacing between neighboring transistors. These  
70 effects can reduce leakage currents between transistors.

- 4 -

The invention can assist all-printed fabrication of display devices. Patterning of the semiconductor layer can be accomplished through use of techniques such as silk screening or stamping. The invention has particular application in the fabrication of large area, flexible lower cost displays that incorporate a microencapsulated electrophoretic display medium.

75

#### Brief Description of the Drawing

The invention, in accordance with preferred and exemplary embodiments, together with further advantages thereof, is more particularly described in the following detailed description, taken in conjunction with the accompanying drawings.

80

In the drawings, like reference characters generally refer to the same parts throughout the different views. Also, the drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating principles of the invention.

Figure 1 shows cross-sectional views of an embodiment of an electronic device at various stages of fabrication.

85

Figure 2a shows a cross-sectional view of an electronic device at an intermediate stage of fabrication that employs screen printing of a destructive agent.

Figure 2b shows a cross-sectional view of an electronic device at an intermediate stage of fabrication that employs stamping of a destructive agent.

Figure 3 shows a cross-sectional view of a display device that utilizes an TFT array fabricated with the process corresponding to the embodiment depicted in Figure 1.

90

Figure 4 shows cross-sectional views of an embodiment of a process for fabricating bottom contact TFT's.

Figure 5 shows a cross-sectional view of a display device that utilizes an TFT array fabricated with the process corresponding to the embodiment depicted in Figure 4.

- 5 -

Figure 6 shows cross-sectional views of an embodiment of a process for fabricating  
95 bottom contact TFT's.

### Detailed Description of the Invention

The present invention relates generally to a method to pattern semiconductor layers, in particular for use in the manufacture of lower cost, large area transistor arrays. The invention is of particular use in the production of displays with a microencapsulated electrophoretic display  
100 medium and mitigates the problem of patterning semiconductor films to reduce leakage currents between neighboring TFT's, in particular those comprising an organic semiconductor film.

#### Patterning by altering a property of an organic semiconductor film via a destructive agent

Referring to Figure 1, two embodiments of a method of patterning an organic semiconductor film 20 are depicted. A substrate 10 is provided (Step 1), comprised of, for  
105 example, a silicon wafer, a polyimide sheet or other polymer sheet. The organic semiconductor film 20 is deposited on the substrate 10 (Step 2). The film 20 comprises, for example, poly(alkyl thiophene), or precursors of pentacene and polythienylenevinylene (PTV), which can be converted into pentacene and PTV semiconductor at elevated temperature. Next, a patterned layer of a destructive agent 100 is deposited adjacent to the organic semiconductor film 20 (Step  
110 3).

The destructive agent 100 is selected for its ability to change a property of the organic semiconductor film 20. Sufficient quantity of the destructive agent 100 is applied so that adjacent portions of the organic semiconductor film 20 have the property changed substantially through the full thickness of the film 20. The property changed can be a chemical, physical or  
15 other property that can have an effect on the electrical properties of the organic semiconductor film 20.

- 6 -

For example, PTV precursor contains a small amount of hydrochloric acid (HCl) as a catalyst during conversion to PTV semiconductor. Therefore, alkaline compounds such as ammonia can be used as the destructive agent. The ammonia concentration can be 2-10 times of that of HCl in the PTV precursor film.

In preferred embodiments, an electrical property of the organic semiconductor film 20 is the changed property. The destructive agent 100 diminishes, for example, the conductivity of the organic semiconductor film 20 in portions that are adjacent to the destructive agent 100. This provides for reduced leakage currents between unaffected portions of the organic semiconductor film 20 which can be used for fabrication of organic TFT's ("OTFT").

Numerous materials can be used for the destructive agent 100. The destructive agent can be chosen to diffuse into the adjacent organic semiconductor film 20 and damage the electrical properties of the organic semiconductor film 20, leaving portions of damaged material 21 of diminished conductivity (Step 4).

Other destructive agents 100 are chosen for their ability to cause gross morphological changes to the adjacent organic semiconductor film 20. For example, the destructive agent can comprise chloroform, toluene, or xylene if the organic semiconductor film 20 comprises poly(alkylthiophene). In this case, adjacent organic semiconductor film 20 material dissolves and redeposits as the solvent dries (Step 4'). This leaves damaged material 22 that has undergone gross morphological changes, typically behaving now as an insulator.

Now referring to Figure 2a and 2b, the destructive agent 100 can be deposited on the organic semiconductor film 20 via various methods. In some preferred embodiments, low cost methods are employed to deposit a patterned film of the destructive agent 100 onto the organic semiconductor film 20. Portions of the organic semiconductor film 20 that are in direct contact with the destructive agent 100 will have their properties damaged.

- 7 -

In one embodiment, a screen 200 is used for patterned deposition of the destructive agent on the organic semiconductor film 20. In another embodiment, a stamp 300 provides patterned deposition of the destructive agent 100. For example, pentacene precursor is soluble in dichloromethane, when an rubber stamp wetted with dichloromethane is brought into contact with pentacene precursor, it partially dissolves the pentacene precursor, therefore, a patterned pentacene can be obtained upon thermal conversion. Other relatively low cost deposition methods can serve to deposit the destructive agent 100, for example, printing processes such as ink jet printing, electrostatic printing processes, and thermal printing.

To assist in the deposition process and control of the destructive agent 100, the destructive agent 100 can comprise a gelling agent. The rheological properties imparted by the gelling agent aid selective placement of, for example, a solvent. The gelling agent can comprise a soluble polymer or a substance that forms extended aggregates.

After a gel-based destructive agent 100 comprising a solvent dissolves neighboring portions of the organic semiconductor film 20, the solvent can then be allowed to dry at ambient temperature or with the application of heat or decreased pressure. The formerly dissolved portions of the organic semiconductor film 20 redeposits in combination with the gelling agent, leaving damaged material 22 with gross morphological changes, typically with no remaining semiconducting properties.

Gross changes in portions of the organic semiconductor 20 can be caused by other materials as the destructive agent 100. For example, chemical reactions through use of, for example, an oxidizing agent can cause portions of the organic semiconductor film 20 to convert to an insulator. Other destructive agents, for example electromagnetic radiation such as UV applied through a contact mask and e-beam applied without a mask, can convert exposed portions of the organic semiconductor film 20 into insulator.



- 8 -

165 In another embodiment, the destructive agent 100 can be deposited first, followed by  
deposit of the organic semiconductor film 20. For example, a patterned layer of poly(ethylene  
glycol) is deposited for use as the destructive agent 100. The layer is patterned either by  
spatially-specific deposition or by blanket deposition followed by removal of selected portions.  
The organic semiconducting film 20 is deposited adjacent to the patterned poly(ethylene glycol)  
170 destructive layer 100. Water is applied, the water dissolving the patterned poly(ethylene glycol)  
destructive layer 100, but not substantially damaging the organic semiconducting film 20. The  
portions of the organic semiconducting film 20 that were adjacent to the patterned poly(ethylene  
glycol) destructive layer 100 become physically detached from the substrate 10 during the  
dissolution of the poly(ethylene glycol) and are removed.

175 Fabrication of displays devices such as liquid crystal or electrophoretic displays, in  
particular microencapsulated electrophoretic displays, can utilize the above method during  
fabrication of arrays of OTFT's for addressing the display medium. Referring to Figure 3, an  
embodiment of an electrophoretic display device comprises: a substrate 10, for example a silicon  
wafer; a gate electrode 40, for example, heavily doped silicon; a dielectric layer 30, for example,  
80 silicon dioxide; source 50 and drain 60 electrodes, for example gold; an organic semiconductor  
film 20, for example poly(alkylthiophene), pentacene, alpha-sexithiophene, or copper  
phthalocyanine ("CuPc"); an electrophoretic display medium assembly 900 comprising an  
electrophoretic display medium 910 and a top electrode 920; and a lamination adhesive 800, for  
example a water-based polyurethane emulsion, where the lamination adhesive is used to attach  
85 the display medium assembly 900 to the organic semiconductor film 20 and other portions of the  
OTFT. In particular, damaged material 21' in portions of the organic semiconductor film provide  
electrical isolation between individual transistors in the OTFT array.

In some embodiments, the array of OTFT's is first separately manufactured from the  
manufacture of the electrophoretic display medium assembly 900. The display medium

- 9 -

190 assembly 900 is comprised, for example, of a microencapsulated electrophoretic display medium printed onto an indium tin oxide ("ITO") coated glass plate. The OTFT array is then bonded, in this embodiment, to the display medium assembly 900 with the lamination adhesive 800.

Patterning with use of a mask

Referring now to Figure 4, a method for manufacturing a transistor utilizes a mask 70 to  
195 assist electrical isolation of neighboring transistors. In one embodiment, the transistor is part of an array of bottom contact transistors. That is, source and drain electrodes lie beneath the semiconductor layer. In one embodiment, the method begins with provision of a substrate 10 (Step 41). Next, the gate electrode 40 is provided on the substrate 10 (Step 42), followed by provision of the dielectric layer 30 (Step 43), preferably a gate dielectric. A source electrode 50  
200 and a drain electrode 60 are deposited onto the dielectric layer 30, opposite to the gate electrode 40 (Step 44).

The mask layer 70 is deposited in a pattern such that the mask layer 70 resides in areas that lie between sites of individual transistors (Step 45). Provision of a semiconductor layer 20' then serves to coat the source and drain electrodes 50, 60, the dielectric layer 30 and the mask 70  
205 (Step 46). Preferably, a thickness of the semiconductor layer 20' is less than a thickness of the mask 70. Preferably, the thickness of the semiconductor layer 20' is in a range of about 1/50 to 1/1000 of the thickness of the mask 70. This thickness disparity can serve to disrupt the continuity of the semiconductor layer 20' between neighboring transistors and make removal of the mask 70 optional. Generally, a bigger thickness disparity provides a better disruption.

10 Even if the continuity of the semiconductor layer 20' is not substantially disrupted by the mask 70, the mask 70 increases the effective physical separation between individual transistors. That is, there is a greater path length through the semiconductor layer 20' from one transistor to the next while passing over the mask 70 than would generally exist without use of the mask 70.

- 10 -

The above described bottom contact process has the further advantage of sparing the vulnerable  
215 semiconductor layer 20' and its interfaces from a solvent used to remove the mask.

One example of a mask material is DuPont 5036 (E.I. du Pont de Nemours and  
Company, Wilmington, DE) which is a solvent-based, screen-printable polymer ink. It can be  
removed by acetone or other solvents.

In some embodiments, relatively simply deposition of the semiconductor layer 20' is  
220 obtained by use of an organic semiconductor or a colloidal dispersion comprising a plurality of  
inorganic semiconducting particles. Solvent processable organic semiconductors like  
polyalkylthiophenes or vacuum evaporated semiconductors such as pentacene can be used. If a  
solution-cast organic semiconductor is used, the solvent used to remove the mask 70 must not be  
a substantial solvent for the organic semiconductor.

225 The semiconductor layer 20' in other embodiments comprises imperfect forms of silicon,  
such as amorphous silicon or polysilicon. Such forms are typically obtained when silicon is  
grown other than directly on a perfect silicon substrate.

Now referring to Figure 5, in some embodiments, arrays of transistors fabricated  
according to the above described processes are advantageously employed in display devices. In  
230 one embodiment, the display assembly 900 is laminated with use of the adhesive 800 to an array  
of transistors fabricated according to the method depicted in Figure 4. Prior to lamination, the  
mask 70 can be partially or fully removed, leaving a portion of mask material or a void 71 in the  
completed display.

The display medium 910 in some embodiments comprises a liquid crystal or an  
35 electrophoretic display medium. Some preferred embodiments employ a microencapsulated  
electrophoretic display medium. Such a medium permits fabrication of an all-printed, large-area  
flexible display.

- 11 -

Referring now to Figure 6, an embodiment of a top contact process for fabricating a transistor or transistor array is described. The substrate 10 (Step 61) has one or more gate electrodes 40 deposited adjacent to it (Step 62). The gate dielectric 30 is deposited adjacent to the gate electrodes 40 and the substrate 10 (Step 63). A patterned mask 70' is then deposited on portions of the dielectric 30 to provide for electrical isolation of individual transistors (Step 64).

Next, a semiconductor layer 20 is deposited adjacent the mask 70' and the portions of exposed dielectric 30 (Step 65). After removal of the mask, a patterned semiconductor layer 20 is obtained (Step 66). Formation of source 50' and drain 60' electrodes completes fabrication of essential features of individual transistors (Step 67).

Various embodiments exist for the materials used and specific geometry of a transistor array. The semiconductor layer 20 comprises either an organic semiconductor or a plurality of colloidal particles. The semiconductor layer 20 is preferably formed with a thickness less than the thickness of the mask 70' to ease removal of the mask along with adjacent portions of the semiconductor layer 20.

The mask in some embodiments is formed through use of a solvent-based polymer. The solvent-based polymer can be deposited, for example, by a printing process followed by evaporation of the solvent. In another embodiment, a polymer is deposited and then cured to form the mask 70'.

Removal of some masks, for example those formed from a solvent-based polymer, can be removed with a solvent, for example acetone. In one embodiment, an organic semiconductor film is patterned by use of a mask 70' as a release layer and a solvent that dissolves the release layer without substantial effect on the organic semiconductor film.

All of the above methods can be advantageously employed in the formation of arrays of polymer-based thin-film transistors in the manufacture of electrophoretic displays. Such displays can take advantage of low cost deposition steps, such as printing of inks, and can be

- 12 -

very flexible, in part though use of flexible, polymer substrates. Further descriptive detail concerning materials and methods utilized in the manufacture of electrophoretic displays is given  
265 in the following.

Method Of Manufacturing An Electrophoretic Display Assembly

In a preferred embodiment, an encapsulated electrophoretic display assembly is manufactured with use of printing or coating steps on a wide variety of flexible substrates. As used herein, the term "printing" includes all forms of printing and coating, including, but not  
270 limited to, pre-metered coatings such as patch die coating, slot or extrusion coating, slide or cascade coating, and curtain coating: roll coating such as knife over roll coating, forward and reverse roll coating, gravure coating, dip coating, spray coating, meniscus coating, spin coating, brush coating, air knife coating, silk screen printing processes, electrostatic printing processes, thermal printing processes, ink jet printing processes and other similar techniques. Thus, the  
275 resulting display can be flexible. Further, because the display medium can be printed (using a variety of methods), the display itself can be made inexpensively.

Further, printing methods can be used to form the electrical connections and other conductive portions of a display. A rear conductor ("rear" referring to a side of a display that is opposite to that viewed by a user) can be either opaque or transparent. This allows the use of a  
280 variety of printed rear conductors, including graphite inks, silver inks, or conductive polymers.

The front conductor ("front" referring to a side of a display that is viewed by a user) must be transparent, but need not have excellent conductivity. Even materials with relatively poor conductivity, though amenable to printing, can be employed, for example conductive colloidal suspensions and conductive polymers such as are commonly used in anti-static applications.

- 13 -

85 A microencapsulated electrophoretic medium, unlike a liquid crystal medium, is amenable to use with a wide number of intrinsically conductive polymer systems, including derivatives of polyaniline, polypyrrole, polythiophene, and polyphenylenevinylene.

In short, the present invention permits a more advantageous use of cost savings allowed by use of printing methods for formation of conducting materials in a display assembly.

90 The following describes in detail various embodiments of materials with applications to the electrophoretic display medium.

#### Materials for Use in Electrophoretic Displays

Useful materials for constructing the above-described encapsulated electrophoretic displays are discussed in detail below. Many of these materials will be known to those skilled in  
95 the art of constructing conventional electrophoretic displays, or those skilled in the art of microencapsulation.

#### A. Particles

There is much flexibility in the choice of particles for use in electrophoretic displays, as described above. For purposes of this invention, a particle is any component that is charged or  
100 capable of acquiring a charge (*i.e.*, has or is capable of acquiring electrophoretic mobility), and, in some cases, this mobility may be zero or close to zero (*i.e.*, the particles will not move). The particles may be neat pigments, dyed (laked) pigments or pigment/polymer composites, or any other component that is charged or capable of acquiring a charge. Typical considerations for the electrophoretic particle are its optical properties, electrical properties, and surface chemistry.  
105 The particles may be organic or inorganic compounds, and they may either absorb light or scatter light. The particles for use in the invention may further include scattering pigments, absorbing pigments and luminescent particles. The particles may be retroreflective, such as corner cubes, or they may be electroluminescent, such as zinc sulfide particles, which emit light when excited

- 14 -

by an AC field, or they may be photoluminescent. Finally, the particles may be surface treated  
310 so as to improve charging or interaction with a charging agent, or to improve dispersibility.

A preferred particle for use in electrophoretic displays of the invention is titania. The  
titania particles may be coated with a metal oxide, such as aluminum oxide or silicon oxide, for  
example. The titania particles may have one, two, or more layers of metal-oxide coating. For  
example, a titania particle for use in electrophoretic displays of the invention may have a coating  
315 of aluminum oxide and a coating of silicon oxide. The coatings may be added to the particle in  
any order.

The electrophoretic particle is usually a pigment, a polymer, a laked pigment, or some  
combination of the above. A neat pigment can be any pigment, and, usually for a light colored  
particle, pigments such as, for example, rutile (titania), anatase (titania), barium sulfate, kaolin,  
320 or zinc oxide are useful. Some typical particles have high refractive indices, high scattering  
coefficients, and low absorption coefficients. Other particles are absorptive, such as carbon  
black or colored pigments used in paints and inks. The pigment should also be insoluble in the  
suspending fluid. Yellow pigments such as diarylide yellow, hansa yellow, and benzidin yellow  
have also found use in similar displays. Any other reflective material can be employed for a  
25 light colored particle, including non-pigment materials, such as metallic particles.

Useful neat pigments include, but are not limited to, PbCrO<sub>4</sub>, Cyan blue GT 55-3295  
(American Cyanamid Company, Wayne, NJ), Cibacron Black BG (Ciba Company, Inc.,  
Newport, DE), Cibacron Turquoise Blue G (Ciba), Cibalon Black BGL (Ciba), Orasol Black  
BRG (Ciba), Orasol Black RBL (Ciba), Acetamine Blac, CBS (E. I. du Pont de Nemours and  
30 Company, Inc., Wilmington, DE), Crocein Scarlet N Ex (du Pont) (27290), Fiber Black VF  
(DuPont) (30235), Luxol Fast Black L (DuPont) (Solv. Black 17), Niroline Base No. 424  
(DuPont) (50415 B), Oil Black BG (DuPont) (Solv. Black 16), Rotalin Black RM (DuPont),  
Sevron Brilliant Red 3 B (DuPont); Basic Black DSC (Dye Specialties, Inc.), Hectolene Black

- 15 -

(Dye Specialties, Inc.), Azosol Brilliant Blue B (GAF, Dyestuff and Chemical Division, Wayne,  
35 NJ) (Solv. Blue 9), Azosol Brilliant Green BA (GAF) (Solv. Green 2), Azosol Fast Brilliant Red  
B (GAF), Azosol Fast Orange RA Conc. (GAF) (Solv. Orange 20), Azosol Fast Yellow GRA  
Conc. (GAF) (13900 A), Basic Black KMPA (GAF), Benzofix Black CW-CF (GAF) (35435),  
Cellitazol BNFV Ex Soluble CF (GAF) (Disp. Black 9), Celliton Fast Blue AF Ex Conc (GAF)  
(Disp. Blue 9), Cyper Black IA (GAF) (Basic Blk. 3), Diamine Black CAP Ex Conc (GAF)  
40 (30235), Diamond Black EAN Hi Con. CF (GAF) (15710), Diamond Black PBBA Ex (GAF)  
(16505); Direct Deep Black EA Ex CF (GAF) (30235), Hansa Yellow G (GAF) (11680);  
Indanthrene Black BBK Powd. (GAF) (59850), Indocarbon CLGS Conc. CF (GAF) (53295),  
Katigen Deep Black NND Hi Conc. CF (GAF) (15711), Rapidogen Black 3 G (GAF) (Azoic  
Blk. 4); Sulphone Cyanine Black BA-CF (GAF) (26370), Zambezi Black VD Ex Conc. (GAF)  
45 (30015); Rubanox Red CP-1495 (The Sherwin-Williams Company, Cleveland, OH) (15630);  
Raven 11 (Columbian Carbon Company, Atlanta, GA), (carbon black aggregates with a particle  
size of about 25  $\mu\text{m}$ ), Statex B-12 (Columbian Carbon Co.) (a furnace black of 33  $\mu\text{m}$  average  
particle size), and chrome green.

Particles may also include laked, or dyed, pigments. Laked pigments are particles that  
50 have a dye precipitated on them or which are stained. Lakes are metal salts of readily soluble  
anionic dyes. These are dyes of azo, triphenylmethane or anthraquinone structure containing one  
or more sulphonic or carboxylic acid groupings. They are usually precipitated by a calcium,  
barium or aluminum salt onto a substrate. Typical examples are peacock blue lake (CI Pigment  
Blue 24) and Persian orange (lake of CI Acid Orange 7), Black M Toner (GAF) (a mixture of  
55 carbon black and black dye precipitated on a lake).

A dark particle of the dyed type may be constructed from any light absorbing material,  
such as carbon black, or inorganic black materials. The dark material may also be selectively  
absorbing. For example, a dark green pigment may be used. Black particles may also be formed



- 16 -

by staining latices with metal oxides, such latex copolymers consisting of any of butadiene,  
360 styrene, isoprene, methacrylic acid, methyl methacrylate, acrylonitrile, vinyl chloride, acrylic  
acid, sodium styrene sulfonate, vinyl acetate, chlorostyrene,  
dimethylaminopropylmethacrylamide, isocyanatoethyl methacrylate and N-  
(isobutoxymethacrylamide), and optionally including conjugated diene compounds such as  
diacrylate, triacrylate, dimethylacrylate and trimethacrylate. Black particles may also be formed  
365 by a dispersion polymerization technique.

In the systems containing pigments and polymers, the pigments and polymers may form  
multiple domains within the electrophoretic particle, or be aggregates of smaller  
pigment/polymer combined particles. Alternatively, a central pigment core may be surrounded  
by a polymer shell. The pigment, polymer, or both can contain a dye. The optical purpose of the  
370 particle may be to scatter light, absorb light, or both. Useful sizes may range from 1 nm up to  
about 100  $\mu\text{m}$ , as long as the particles are smaller than the bounding capsule. In a preferred  
embodiment, the density of the electrophoretic particle may be substantially matched to that of  
the suspending (*i.e.*, electrophoretic) fluid. As defined herein, a suspending fluid has a density  
that is "substantially matched" to the density of the particle if the difference in their respective  
375 densities is between about zero and about two g/ml. This difference is preferably between about  
zero and about 0.5 g/ml.

Useful polymers for the particles include, but are not limited to: polystyrene,  
polyethylene, polypropylene, phenolic resins, Du Pont Elvax resins (ethylene-vinyl acetate  
copolymers), polyesters, polyacrylates, polymethacrylates, ethylene acrylic acid or methacrylic  
380 acid copolymers (Nucel Resins - DuPont, Primacor Resins- Dow Chemical), acrylic copolymers  
and terpolymers (Elvacite Resins, DuPont) and PMMA. Useful materials for homopolymer /  
pigment phase separation in high shear melt include, but are not limited to, polyethylene,  
polypropylene, polymethylmethacrylate, polyisobutylmethacrylate, polystyrene, polybutadiene,

- 17 -

polyisoprene, polyisobutylene, polylauryl methacrylate, polystearyl methacrylate, polyisobornyl  
185 methacrylate, poly-t-butyl methacrylate, polyethyl methacrylate, polymethyl acrylate, polyethyl  
acrylate, polyacrylonitrile, and copolymers of two or more of these materials. Some useful  
pigment/polymer complexes that are commercially available include, but are not limited to,  
Process Magenta PM 1776 (Magruder Color Company, Inc., Elizabeth, NJ), Methyl Violet PMA  
VM6223 (Magruder Color Company, Inc., Elizabeth, NJ), and Naphthol FGR RF6257  
90 (Magruder Color Company, Inc., Elizabeth, NJ).

The pigment-polymer composite may be formed by a physical process, (*e.g.*, attrition or  
ball milling), a chemical process (*e.g.*, microencapsulation or dispersion polymerization), or any  
other process known in the art of particle production. From the following non-limiting  
examples, it may be seen that the processes and materials for both the fabrication of particles and  
95 the charging thereof are generally derived from the art of liquid toner, or liquid immersion  
development. Thus any of the known processes from liquid development are particularly, but  
not exclusively, relevant.

New and useful electrophoretic particles may still be discovered, but a number of  
particles already known to those skilled in the art of electrophoretic displays and liquid toners  
00 can also prove useful. In general, the polymer requirements for liquid toners and encapsulated  
electrophoretic inks are similar, in that the pigment or dye must be easily incorporated therein,  
either by a physical, chemical, or physicochemical process, may aid in the colloidal stability, and  
may contain charging sites or may be able to incorporate materials which contain charging sites.  
One general requirement from the liquid toner industry that is not shared by encapsulated  
95 electrophoretic inks is that the toner must be capable of "fixing" the image, *i.e.*, heat fusing  
together to create a uniform film after the deposition of the toner particles.

Typical manufacturing techniques for particles are drawn from the liquid toner and other  
arts and include ball milling, attrition, jet milling, *etc.* The process will be illustrated for the case

- 18 -

of a pigmented polymeric particle. In such a case the pigment is compounded in the polymer,  
usually in some kind of high shear mechanism such as a screw extruder. The composite material  
is then (wet or dry) ground to a starting size of around 10  $\mu\text{m}$ . It is then dispersed in a carrier  
liquid, for example ISOPAR<sup>®</sup> (Exxon, Houston, TX), optionally with some charge control  
agent(s), and milled under high shear for several hours down to a final particle size and/or size  
distribution.

Another manufacturing technique for particles drawn from the liquid toner field is to add  
the polymer, pigment, and suspending fluid to a media mill. The mill is started and  
simultaneously heated to temperature at which the polymer swells substantially with the solvent.  
This temperature is typically near 100°C. In this state, the pigment is easily encapsulated into  
the swollen polymer. After a suitable time, typically a few hours, the mill is gradually cooled  
back to ambient temperature while stirring. The milling may be continued for some time to  
achieve a small enough particle size, typically a few microns in diameter. The charging agents  
may be added at this time. Optionally, more suspending fluid may be added.

Chemical processes such as dispersion polymerization, mini- or micro-emulsion  
polymerization, suspension polymerization precipitation, phase separation, solvent evaporation,  
*in situ* polymerization, seeded emulsion polymerization, or any process which falls under the  
general category of microencapsulation may be used. A typical process of this type is a phase  
separation process wherein a dissolved polymeric material is precipitated out of solution onto a  
dispersed pigment surface through solvent dilution, evaporation, or a thermal change. Other  
processes include chemical means for staining polymeric latices, for example with metal oxides  
or dyes.

#### B. Suspending Fluid

The suspending fluid containing the particles can be chosen based on properties such as  
density, refractive index, and solubility. A preferred suspending fluid has a low dielectric

- 19 -

constant (about 2), high volume resistivity (about  $10^{15}$  ohm-cm), low viscosity (less than 5 cst),  
35 low toxicity and environmental impact, low water solubility (less than 10 ppm), high specific  
gravity (greater than 1.5), a high boiling point (greater than 90°C), and a low refractive index  
(less than 1.2).

The choice of suspending fluid may be based on concerns of chemical inertness, density  
matching to the electrophoretic particle, or chemical compatibility with both the electrophoretic  
40 particle and bounding capsule. The viscosity of the fluid should be low when you want the  
particles to move. The refractive index of the suspending fluid may also be substantially  
matched to that of the particles. As used herein, the refractive index of a suspending fluid "is  
substantially matched" to that of a particle if the difference between their respective refractive  
indices is between about zero and about 0.3, and is preferably between about 0.05 and about 0.2.

15 Additionally, the fluid may be chosen to be a poor solvent for some polymers, which is  
advantageous for use in the fabrication of microparticles because it increases the range of  
polymeric materials useful in fabricating particles of polymers and pigments. Organic solvents,  
such as halogenated organic solvents, saturated linear or branched hydrocarbons, silicone oils,  
and low molecular weight halogen-containing polymers are some useful suspending fluids. The  
0 suspending fluid may comprise a single fluid. The fluid will, however, often be a blend of more  
than one fluid in order to tune its chemical and physical properties. Furthermore, the fluid may  
contain surface modifiers to modify the surface energy or charge of the electrophoretic particle  
or bounding capsule. Reactants or solvents for the microencapsulation process (oil soluble  
monomers, for example) can also be contained in the suspending fluid. Charge control agents  
5 can also be added to the suspending fluid.

Useful organic solvents include, but are not limited to, epoxides, such as, for example,  
decane epoxide and dodecane epoxide; vinyl ethers, such as, for example, cyclohexyl vinyl ether  
and Decave<sup>®</sup> (International Flavors & Fragrances, Inc., New York, NY); and aromatic

- 20 -

hydrocarbons, such as, for example, toluene and naphthalene. Useful halogenated organic  
460 solvents include, but are not limited to, tetrafluorodibromoethylene, tetrachloroethylene,  
trifluorochloroethylene, 1,2,4-trichlorobenzene, carbon tetrachloride. These materials have high  
densities. Useful hydrocarbons include, but are not limited to, dodecane, tetradecane, the  
aliphatic hydrocarbons in the Isopar<sup>®</sup> series (Exxon, Houston, TX), Norpar<sup>®</sup> (series of normal  
paraffinic liquids), Shell-Sol<sup>®</sup> (Shell, Houston, TX), and Sol-Trol<sup>®</sup> (Shell), naphtha, and other  
465 petroleum solvents. These materials usually have low densities. Useful examples of silicone  
oils include, but are not limited to, octamethyl cyclosiloxane and higher molecular weight cyclic  
siloxanes, poly (methyl phenyl siloxane), hexamethyldisiloxane, and polydimethylsiloxane.  
These materials usually have low densities. Useful low molecular weight halogen-containing  
polymers include, but are not limited to, poly(chlorotrifluoroethylene) polymer (Halogenated  
170 hydrocarbon Inc., River Edge, NJ), Galden<sup>®</sup> (a perfluorinated ether from Ausimont, Morristown,  
NJ), or Krytox<sup>®</sup> from DuPont (Wilmington, DE). In a preferred embodiment, the suspending  
fluid is a poly(chlorotrifluoroethylene) polymer. In a particularly preferred embodiment, this  
polymer has a degree of polymerization from about 2 to about 10. Many of the above materials  
are available in a range of viscosities, densities, and boiling points.

75 The fluid must be capable of being formed into small droplets prior to a capsule being  
formed. Processes for forming small droplets include flow-through jets, membranes, nozzles, or  
orifices, as well as shear-based emulsifying schemes. The formation of small drops may be  
assisted by electrical or sonic fields. Surfactants and polymers can be used to aid in the  
stabilization and emulsification of the droplets in the case of an emulsion type encapsulation. A  
80 preferred surfactant for use in displays of the invention is sodium dodecylsulfate.

It can be advantageous in some displays for the suspending fluid to contain an optically  
absorbing dye. This dye must be soluble in the fluid, but will generally be insoluble in the other  
components of the capsule. There is much flexibility in the choice of dye material. The dye can

- 21 -

be a pure compound, or blends of dyes to achieve a particular color, including black. The dyes  
485 can be fluorescent, which would produce a display in which the fluorescence properties depend  
on the position of the particles. The dyes can be photoactive, changing to another color or  
becoming colorless upon irradiation with either visible or ultraviolet light, providing another  
means for obtaining an optical response. Dyes could also be polymerizable, forming a solid  
absorbing polymer inside the bounding shell.

490 There are many dyes that can be chosen for use in encapsulated electrophoretic display.  
Properties important here include light fastness, solubility in the suspending liquid, color, and  
cost. These are generally from the class of azo, anthraquinone, and triphenylmethane type dyes  
and may be chemically modified so as to increase the solubility in the oil phase and reduce the  
adsorption by the particle surface.

195 A number of dyes already known to those skilled in the art of electrophoretic displays  
will prove useful. Useful azo dyes include, but are not limited to: the Oil Red dyes, and the  
Sudan Red and Sudan Black series of dyes. Useful anthraquinone dyes include, but are not  
limited to: the Oil Blue dyes, and the Macrolex Blue series of dyes. Useful triphenylmethane  
dyes include, but are not limited to, Michler's hydrol, Malachite Green, Crystal Violet, and  
600 Auramine O.

### C. Charge Control Agents and Particle Stabilizers

Charge control agents are used to provide good electrophoretic mobility to the  
electrophoretic particles. Stabilizers are used to prevent agglomeration of the electrophoretic  
particles, as well as prevent the electrophoretic particles from irreversibly depositing onto the  
05 capsule wall. Either component can be constructed from materials across a wide range of  
molecular weights (low molecular weight, oligomeric, or polymeric), and may be pure or a  
mixture. In particular, suitable charge control agents are generally adapted from the liquid toner  
art. The charge control agent used to modify and/or stabilize the particle surface charge is

- 22 -

applied as generally known in the arts of liquid toners, electrophoretic displays, non-aqueous  
510 paint dispersions, and engine-oil additives. In all of these arts, charging species may be added to  
non-aqueous media in order to increase electrophoretic mobility or increase electrostatic  
stabilization. The materials can improve steric stabilization as well. Different theories of  
charging are postulated, including selective ion adsorption, proton transfer, and contact  
electrification.

515 An optional charge control agent or charge director may be used. These constituents  
typically consist of low molecular weight surfactants, polymeric agents, or blends of one or more  
components and serve to stabilize or otherwise modify the sign and/or magnitude of the charge  
on the electrophoretic particles. The charging properties of the pigment itself may be accounted  
for by taking into account the acidic or basic surface properties of the pigment, or the charging  
520 sites may take place on the carrier resin surface (if present), or a combination of the two.

Additional pigment properties which may be relevant are the particle size distribution, the  
chemical composition, and the lightfastness. The charge control agent used to modify and/or  
stabilize the particle surface charge is applied as generally known in the arts of liquid toners,  
electrophoretic displays, non-aqueous paint dispersions, and engine-oil additives. In all of these  
25 arts, charging species may be added to non-aqueous media in order to increase electrophoretic  
mobility or increase electrostatic stabilization. The materials can improve steric stabilization as  
well. Different theories of charging are postulated, including selective ion adsorption, proton  
transfer, and contact electrification.

Charge adjuvants may also be added. These materials increase the effectiveness of the  
30 charge control agents or charge directors. The charge adjuvant may be a polyhydroxy compound  
or an aminoalcohol compound, which are preferably soluble in the suspending fluid in an amount  
of at least 2% by weight. Examples of polyhydroxy compounds which contain at least two  
hydroxyl groups include, but are not limited to, ethylene glycol, 2,4,7,9-tetramethyl-decane-4,7-

- 23 -

diol, poly(propylene glycol), pentaethylene glycol, tripropylene glycol, triethylene glycol,  
15 glycerol, pentaerythritol, glycerol tris(12-hydroxystearate), propylene glycerol  
monohydroxystearate, and ethylene glycol monohydroxystearate. Examples of aminoalcohol  
compounds which contain at least one alcohol function and one amine function in the same  
molecule include, but are not limited to, triisopropanolamine, triethanolamine, ethanolamine, 3-  
amino-1-propanol, o-aminophenol, 5-amino-1-pentanol, and tetrakis(2-hydroxyethyl)ethylene-  
0 diamine. The charge adjuvant is preferably present in the suspending fluid in an amount of about  
1 to about 100 mg/g of the particle mass, and more preferably about 50 to about 200 mg/g.

The surface of the particle may also be chemically modified to aid dispersion, to improve  
surface charge, and to improve the stability of the dispersion, for example. Surface modifiers  
include organic siloxanes, organohalogen silanes and other functional silane coupling agents  
5 (Dow Corning® Z-6070, Z-6124, and 3 additive, Midland, MI); organic titanates and zirconates  
(Tyzor® TOT, TBT, and TE Series, DuPont, Wilmington, DE); hydrophobing agents, such as  
long chain (C12 to C50) alkyl and alkyl benzene sulphonic acids, fatty amines or diamines and  
their salts or quarternary derivatives; and amphipathic polymers which can be covalently bonded  
to the particle surface.

0 In general, it is believed that charging results as an acid-base reaction between some  
moiety present in the continuous phase and the particle surface. Thus useful materials are those  
which are capable of participating in such a reaction, or any other charging reaction as known in  
the art.

Different non-limiting classes of charge control agents which are useful include organic  
5 sulfates or sulfonates, metal soaps, block or comb copolymers, organic amides, organic  
zwitterions, and organic phosphates and phosphonates. Useful organic sulfates and sulfonates  
include, but are not limited to, sodium bis(2-ethyl hexyl) sulfosuccinate, calcium dodecyl  
benzene sulfonate, calcium petroleum sulfonate, neutral or basic barium dinonylnaphthalene



- 24 -

sulfonate, neutral or basic calcium dinonylnaphthalene sulfonate, dodecylbenzenesulfonic acid  
560 sodium salt, and ammonium lauryl sulphate. Useful metal soaps include, but are not limited to,  
basic or neutral barium petronate, calcium petronate, Co-, Ca-, Cu-, Mn-, Ni-, Zn-, and Fe- salts  
of naphthenic acid, Ba-, Al-, Zn-, Cu-, Pb-, and Fe- salts of stearic acid, divalent and trivalent  
metal carboxylates, such as aluminum tristearate, aluminum octanoate, lithium heptanoate, iron  
stearate, iron distearate, barium stearate, chromium stearate, magnesium octanoate, calcium  
65 stearate, iron naphthenate, and zinc naphthenate, Mn- and Zn- heptanoate, and Ba-, Al-, Co-,  
Mn-, and Zn- octanoate. Useful block or comb copolymers include, but are not limited to, AB  
diblock copolymers of (A) polymers of 2-(N,N)-dimethylaminoethyl methacrylate quaternized  
with methyl-p-toluenesulfonate and (B) poly-2-ethylhexyl methacrylate, and comb graft  
copolymers with oil soluble tails of poly (12-hydroxystearic acid) and having a molecular weight  
70 of about 1800, pendant on an oil-soluble anchor group of poly (methyl methacrylate-methacrylic  
acid). Useful organic amides include, but are not limited to, polyisobutylene succinimides such  
as OLOA 371 and 1200, and N-vinyl pyrrolidone polymers. Useful organic zwitterions include,  
but are not limited to, lecithin. Useful organic phosphates and phosphonates include, but are not  
limited to, the sodium salts of phosphated mono- and di-glycerides with saturated and  
75 unsaturated acid substituents.

Particle dispersion stabilizers may be added to prevent particle flocculation or attachment  
to the capsule walls. For the typical high resistivity liquids used as suspending fluids in  
electrophoretic displays, nonaqueous surfactants may be used. These include, but are not limited  
to, glycol ethers, acetylenic glycols, alkanolamides, sorbitol derivatives, alkyl amines, quaternary  
80 amines, imidazolines, dialkyl oxides, and sulfosuccinates.

#### D. Encapsulation

There is a long and rich history to encapsulation, with numerous processes and polymers

- 25 -

having proven useful in creating capsules. Encapsulation of the internal phase may be accomplished in a number of different ways. Numerous suitable procedures for microencapsulation are detailed in both *Microencapsulation, Processes and Applications*, (I. E. Vandegaer, ed.), Plenum Press, New York, NY (1974) and Gutcho, *Microcapsules and Microencapsulation Techniques*, Nuyes Data Corp., Park Ridge, N.J. (1976). The processes fall into several general categories, all of which can be applied to the present invention: interfacial polymerization, *in situ* polymerization, physical processes, such as coextrusion and other phase separation processes, in-liquid curing, and simple/complex coacervation.

Numerous materials and processes should prove useful in formulating displays of the present invention. Useful materials for simple coacervation processes include, but are not limited to, gelatin, polyvinyl alcohol, polyvinyl acetate, and cellulosic derivatives, such as, for example, carboxymethylcellulose. Useful materials for complex coacervation processes include, but are not limited to, gelatin, acacia, carageenan, carboxymethylcellulose, hydrolyzed styrene anhydride copolymers, agar, alginate, casein, albumin, methyl vinyl ether co-maleic anhydride, and cellulose phthalate. Useful materials for phase separation processes include, but are not limited to, polystyrene, PMMA, polyethyl methacrylate, polybutyl methacrylate, ethyl cellulose, polyvinyl pyridine, and poly acrylonitrile. Useful materials for *in situ* polymerization processes include, but are not limited to, polyhydroxyamides, with aldehydes, melamine, or urea and formaldehyde; water-soluble oligomers of the condensate of melamine, or urea and formaldehyde; and vinyl monomers, such as, for example, styrene, MMA and acrylonitrile. Finally, useful materials for interfacial polymerization processes include, but are not limited to, diacyl chlorides, such as, for example, sebacoyl, adipoyl, and di- or poly- amines or alcohols, and isocyanates. Useful emulsion polymerization materials may include, but are not limited to, styrene, vinyl acetate, acrylic acid, butyl acrylate, t-butyl acrylate, methyl methacrylate, and butyl methacrylate.

- 26 -

Capsules produced may be dispersed into a curable carrier, resulting in an ink which may be printed or coated on large and arbitrarily shaped or curved surfaces using conventional printing and coating techniques.

In the context of the present invention, one skilled in the art will select an encapsulation procedure and wall material based on the desired capsule properties. These properties include the distribution of capsule radii; electrical, mechanical, diffusion, and optical properties of the capsule wall; and chemical compatibility with the internal phase of the capsule.

The capsule wall generally has a high electrical resistivity. Although it is possible to use walls with relatively low resistivities, this may limit performance in requiring relatively higher addressing voltages. The capsule wall should also be mechanically strong (although if the finished capsule powder is to be dispersed in a curable polymeric binder for coating, mechanical strength is not as critical). The capsule wall should generally not be porous. If, however, it is desired to use an encapsulation procedure that produces porous capsules, these can be overcoated in a post-processing step (*i.e.*, a second encapsulation). Moreover, if the capsules are to be dispersed in a curable binder, the binder will serve to close the pores. The capsule walls should be optically clear. The wall material may, however, be chosen to match the refractive index of the internal phase of the capsule (*i.e.*, the suspending fluid) or a binder in which the capsules are to be dispersed. For some applications (*e.g.*, interposition between two fixed electrodes), monodispersed capsule radii are desirable.

An encapsulation procedure involves a polymerization between urea and formaldehyde in an aqueous phase of an oil/water emulsion in the presence of a negatively charged, carboxyl-substituted, linear hydrocarbon polyelectrolyte material. The resulting capsule wall is a urea/formaldehyde copolymer, which discretely encloses the internal phase. The capsule is clear, mechanically strong, and has good resistivity properties.

- 27 -

The related technique of *in situ* polymerization utilizes an oil/water emulsion, which is formed by dispersing the electrophoretic composition (*i.e.*, the dielectric liquid containing a suspension of the pigment particles) in an aqueous environment. The monomers polymerize to form a polymer with higher affinity for the internal phase than for the aqueous phase, thus condensing around the emulsified oily droplets. In one especially useful *in situ* polymerization processes, urea and formaldehyde condense in the presence of poly(acrylic acid) (See, *e.g.*, U.S. Patent No. 4,001,140). In other useful process, any of a variety of cross-linking agents borne in aqueous solution is deposited around microscopic oil droplets. Such cross-linking agents include aldehydes, especially formaldehyde, glyoxal, or glutaraldehyde; alum; zirconium salts; and polyisocyanates. The entire disclosures of the 4,001,140 and 4,273,672 patents are hereby incorporated by reference herein.

The coacervation approach also utilizes an oil/water emulsion. One or more colloids are coacervated (*i.e.*, agglomerated) out of the aqueous phase and deposited as shells around the oily droplets through control of temperature, pH and/or relative concentrations, thereby creating the microcapsule. Materials suitable for coacervation include gelatins and gum arabic.

The interfacial polymerization approach relies on the presence of an oil-soluble monomer in the electrophoretic composition, which once again is present as an emulsion in an aqueous phase. The monomers in the minute hydrophobic droplets react with a monomer introduced into the aqueous phase, polymerizing at the interface between the droplets and the surrounding aqueous medium and forming shells around the droplets. Although the resulting walls are relatively thin and may be permeable, this process does not require the elevated temperatures characteristic of some other processes, and therefore affords greater flexibility in terms of choosing the dielectric liquid.

Coating aids can be used to improve the uniformity and quality of the coated or printed

- 28 -

electrophoretic ink material. Wetting agents are typically added to adjust the interfacial tension at the coating/substrate interface and to adjust the liquid/air surface tension. Wetting agents include, but are not limited to, anionic and cationic surfactants, and nonionic species, such as silicone or fluoropolymer based materials. Dispersing agents may be used to modify the interfacial tension between the capsules and binder, providing control over flocculation and particle settling.

Surface tension modifiers can be added to adjust the air/ink interfacial tension.

Polysiloxanes are typically used in such an application to improve surface leveling while minimizing other defects within the coating. Surface tension modifiers include, but are not limited to, fluorinated surfactants, such as, for example, the Zonyl® series from DuPont (Wilmington, DE), the Fluorod® series from 3M (St. Paul, MN), and the fluoroakyl series from Autochem (Glen Rock, NJ); siloxanes, such as, for example, Silwet® from Union Carbide (Danbury, CT); and polyethoxy and polypropoxy alcohols. Antifoams, such as silicone and silicone-free polymeric materials, may be added to enhance the movement of air from within the ink to the surface and to facilitate the rupture of bubbles at the coating surface. Other useful antifoams include, but are not limited to, glyceryl esters, polyhydric alcohols, compounded antifoams, such as oil solutions of alkyl benzenes, natural fats, fatty acids, and metallic soaps, and silicone antifoaming agents made from the combination of dimethyl siloxane polymers and silica. Stabilizers such as uv-absorbers and antioxidants may also be added to improve the lifetime of the ink.

Other additives to control properties like coating viscosity and foaming can also be used in the coating fluid. Stabilizers (UV-absorbers, antioxidants) and other additives which could prove useful in practical materials.

#### E. Binder Material

The binder is used as a non-conducting, adhesive medium supporting and protecting the

- 29 -

capsules, as well as binding the electrode materials to the capsule dispersion. Binders are available in many forms and chemical types. Among these are water-soluble polymers, water-borne polymers, oil-soluble polymers, thermoset and thermoplastic polymers, and radiation-cured polymers.

85 Among the water-soluble polymers are the various polysaccharides, the polyvinyl alcohols, N-methylpyrrolidone, N-vinylpyrrolidone, the various Carbowax<sup>®</sup> species (Union Carbide, Danbury, CT), and poly-2-hydroxyethylacrylate.

The water-dispersed or water-borne systems are generally latex compositions, typified by the Neorez<sup>®</sup> and Neocryl<sup>®</sup> resins (Zeneca Resins, Wilmington, MA), Acrysol<sup>®</sup> (Rohm and Haas, Philadelphia, PA), Bayhydrol<sup>®</sup> (Bayer, Pittsburgh, PA), and the Cytec Industries (West Paterson, NJ) HP line. These are generally latices of polyurethanes, occasionally compounded with one or more of the acrylics, polyesters, polycarbonates or silicones, each lending the final cured resin in a specific set of properties defined by glass transition temperature, degree of "tack," softness, clarity, flexibility, water permeability and solvent resistance, elongation modulus and tensile strength, thermoplastic flow, and solids level. Some water-borne systems can be mixed with reactive monomers and catalyzed to form more complex resins. Some can be further cross-linked by the use of a crosslinking reagent, such as an aziridine, for example, which reacts with carboxyl groups.

A typical application of a water-borne resin and aqueous capsules follows. A volume of particles is centrifuged at low speed to separate excess water. After a given centrifugation process, for example 10 minutes at 60 x g, the capsules are found at the bottom of the centrifuge tube, while the water portion is at the top. The water portion is carefully removed (by decanting or pipetting). The mass of the remaining capsules is measured, and a mass of resin is added such that the mass of resin is between one eighth and one tenth of the weight of the capsules. This mixture is gently mixed on an oscillating mixer for approximately one half hour. After about

- 30 -

one half hour, the mixture is ready to be coated onto the appropriate substrate.

The thermoset systems are exemplified by the family of epoxies. These binary systems can vary greatly in viscosity, and the reactivity of the pair determines the "pot life" of the mixture. If the pot life is long enough to allow a coating operation, capsules may be coated in an ordered arrangement in a coating process prior to the resin curing and hardening.

Thermoplastic polymers, which are often polyesters, are molten at high temperatures. A typical application of this type of product is hot-melt glue. A dispersion of heat-resistant capsules could be coated in such a medium. The solidification process begins during cooling, and the final hardness, clarity and flexibility are affected by the branching and molecular weight of the polymer.

Oil or solvent-soluble polymers are often similar in composition to the water-borne system, with the obvious exception of the water itself. The latitude in formulation for solvent systems is enormous, limited only by solvent choices and polymer solubility. Of considerable concern in solvent-based systems is the viability of the capsule itself - the integrity of the capsule wall cannot be compromised in any way by the solvent.

Radiation cure resins are generally found among the solvent-based systems. Capsules may be dispersed in such a medium and coated, and the resin may then be cured by a timed exposure to a threshold level of ultraviolet radiation, either long or short wavelength. As in all cases of curing polymer resins, final properties are determined by the branching and molecular weights of the monomers, oligomers and crosslinkers.

A number of "water-reducible" monomers and oligomers are, however, marketed. In the strictest sense, they are not water soluble, but water is an acceptable diluent at low concentrations and can be dispersed relatively easily in the mixture. Under these circumstances, water is used to reduce the viscosity (initially from thousands to hundreds of thousands centipoise). Water-based capsules, such as those made from a protein or polysaccharide

- 31 -

material, for example, could be dispersed in such a medium and coated, provided the viscosity could be sufficiently lowered. Curing in such systems is generally by ultraviolet radiation.

While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in  
35 form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.



- 32 -

CLAIMS

What is claimed is:

- 1 1. A process for forming a pattern in a semiconductor film comprising the steps of:
  - 2 a) providing a substrate;
  - 3 b) providing an organic semiconductor film adjacent the substrate; and
  - 4 c) providing a destructive agent adjacent selected portions of the organic semiconductor  
5 film, the destructive agent changing a property of the selected portions of the organic  
6 semiconductor film such that the property of the selected portions of the organic  
7 semiconductor film differs from the property of a remaining portion of the organic  
8 semiconductor film, wherein the property of the selected portions is changed  
9 substantially through the full thickness of the organic semiconductor film.
- 1 2. The process of claim 1 further comprising the step of d) providing at least one of a  
2 conductive element and an insulative element to provide a circuit.
- 1 3. The process of claim 1 wherein the destructive agent changes an electrical property of  
2 selected portions of the organic semiconductor film.
- 1 4. The process of claim 1 wherein step c) comprises dissolution of the selected portions of the  
2 organic semiconductor film.
- 1 5. The process of claim 4 wherein the destructive agent comprises a solvent.
- 1 6. The process of claim 5 wherein the destructive agent comprises a solvent and a gelling agent.
- 1 7. The process of claim 5 further comprising the step of d) evaporating the solvent after  
2 dissolving the organic semiconductor film.
- 1 8. The process of claim 1 wherein step c) comprises providing the destructive agent through a  
2 printing process.
- 1 9. The process of claim 8 wherein step c) comprises providing the destructive agent through a  
2 screen printing process.
- 1 10. The process of claim 1 wherein step c) comprises providing the destructive agent through a  
2 stamping process.
- 1 11. The process of claim 1 wherein the organic semiconductor layer comprises poly(alkyl  
2 thiophene) and the destructive agent comprises one of chloroform, toluene, and xylene.

- 33 -

- 1 12. A method for manufacturing a transistor comprising the steps of:
- 2 a) providing a substrate;
- 3 b) providing a gate electrode adjacent the substrate;
- 4 a) providing a gate dielectric adjacent the substrate and the gate electrode;
- 5 b) providing a source electrode and a drain electrode adjacent the gate dielectric;
- 6 c) providing a mask adjacent the gate dielectric in a pattern such that the source
- 7 electrode, the drain electrode, and a portion of the gate dielectric remain exposed; and
- 8 d) providing a semiconductor layer comprising one of an organic semiconductor and a
- 9 plurality of inorganic colloidal particles, adjacent the source electrode, the drain
- 0 electrode, the portion of the gate dielectric and the mask, thereby forming the
- 1 transistor, the semiconductor layer having a thickness less than a thickness of the
- 2 mask.
- 1 13. The method of claim 12 wherein step f) comprises printing the mask by f1) providing a
- 2 solvent-based polymer adjacent the gate dielectric and f2) evaporating the solvent.
- 1 14. The method of claim 12 further comprising providing an electronic display medium
- 2 comprising a plurality of microcapsules, each capsule comprising one of electrophoretic
- 3 particles, suspended particles and bichromal sphere, and providing the semiconductor layer
- 4 near the display medium for addressing the display medium.
- 1 15. The method of claim 12 further comprising providing a liquid crystal display medium and
- 2 providing the semiconductor layer near the display medium for addressing the display
- 3 medium.
- 1 16. The method of claim 12 wherein step f) comprises f1) printing a mask comprising polymer
- 2 adjacent the gate dielectric and f2) curing the polymer.
- 1 17. The method of claim 12 wherein step g) comprises providing a semiconductor layer having a
- 2 thickness of 1/50 to 1/1000 of a thickness of the mask.
- 1 18. A method for manufacturing a transistor comprising the steps of:
- 2 a) providing a substrate;
- 3 b) providing a gate electrode adjacent the substrate;
- 4 c) providing a gate dielectric adjacent the gate electrode and the substrate;

- 34 -

- d) printing a mask adjacent the gate dielectric in a pattern such that a portion of gate dielectric remains exposed;
- e) providing a semiconductor layer comprising one of an organic semiconductor and a plurality of inorganic colloidal particles, adjacent the mask and the portion of the gate dielectric, the semiconductor layer having a thickness less than a thickness of the mask;
- f) removing the mask; and
- g) forming a source electrode and a drain electrode adjacent the semiconductor layer and the gate dielectric, thereby forming the transistor.

19. The method of claim 18 further comprising providing an electronic display medium comprising a plurality of microcapsules, each capsule comprising one of electrophoretic particles, suspended particles and bichromal sphere, and providing the semiconductor layer near the display medium for addressing the display medium.

20. The method of claim 18 further comprising providing a liquid crystal display medium and providing the semiconductor layer near the display medium for addressing the display medium.

21. The method of claim 18 wherein step d) comprises printing the mask by d1) providing a solvent-based polymer adjacent the gate dielectric and d2) evaporating the solvent.

22. The method of claim 18 wherein step d) comprises d1) printing the mask comprising a polymer adjacent the gate dielectric and d2) curing the polymer.

23. The method of claim 18 wherein step f) comprises removing the mask using a solvent.

24. The method of claim 23 wherein the solvent comprises acetone.

25. The method of claim 18 wherein step e) comprises providing a semiconductor layer having a thickness of about 1/50 to 1/1000 of a thickness of the mask.

26. A process for forming a pattern in a semiconductor film comprising the steps of:

- a) providing a substrate;
- b) providing a release layer adjacent selected portions of the substrate;
- c) providing an organic semiconductor film adjacent the release layer and the substrate; and

- 35 -

- 4 d) exposing the release layer to a solvent which dissolves the release layer without  
5 dissolving the organic semiconductor film, thereby removing the release layer and the  
6 organic semiconductor film adjacent the release layer without removing the organic  
7 semiconductor film adjacent the substrate.

1/5

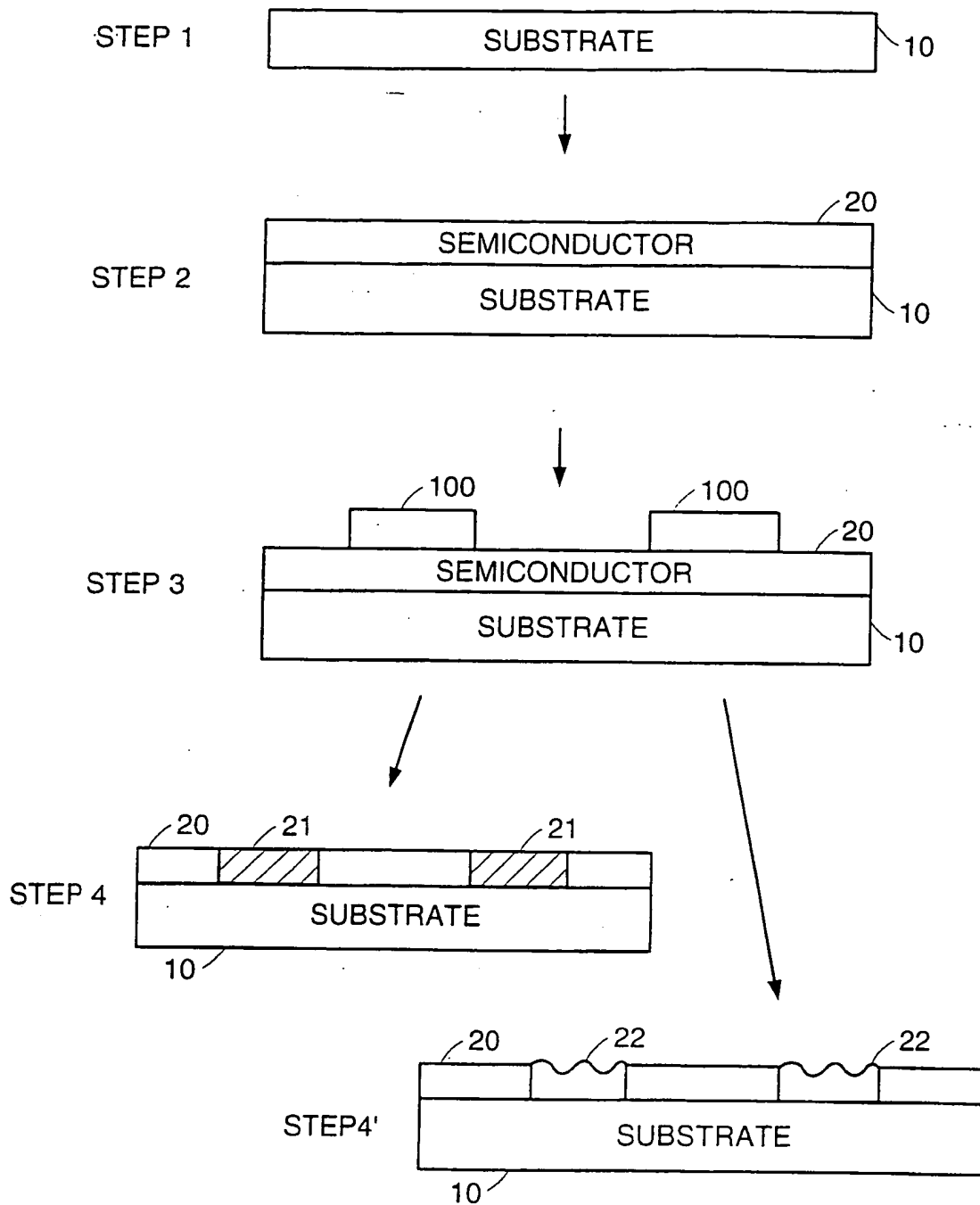


FIG. 1

2/5

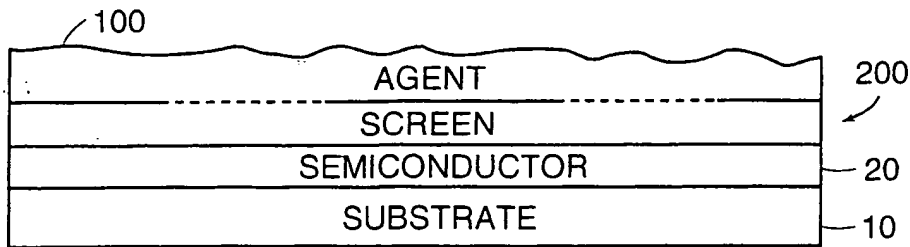


FIG. 2a

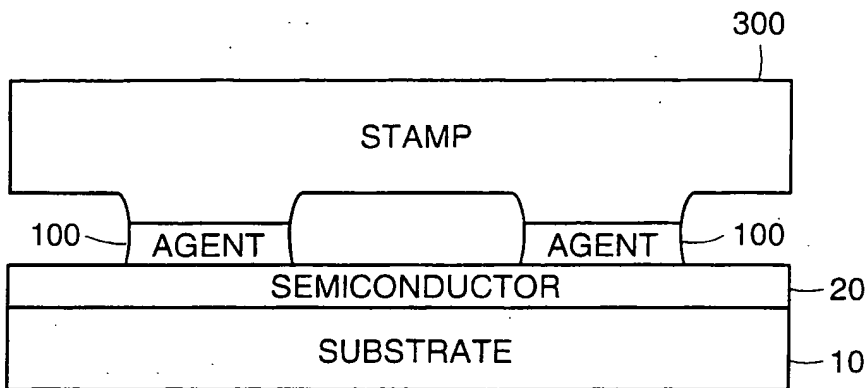


FIG. 2b

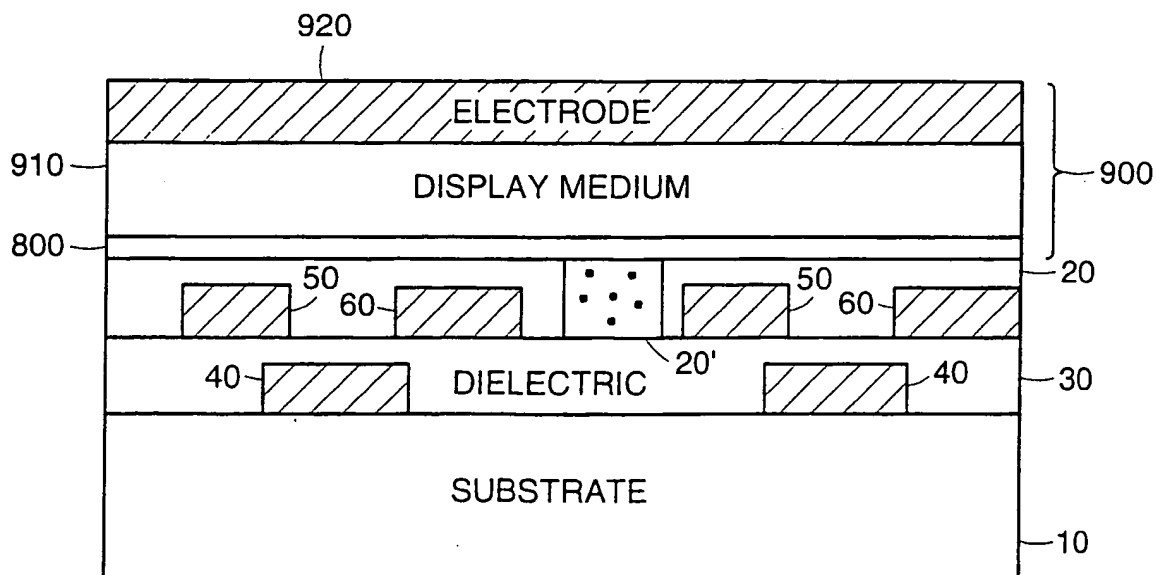


FIG. 3

3/5

BOTTOM CONTACT PROCESS

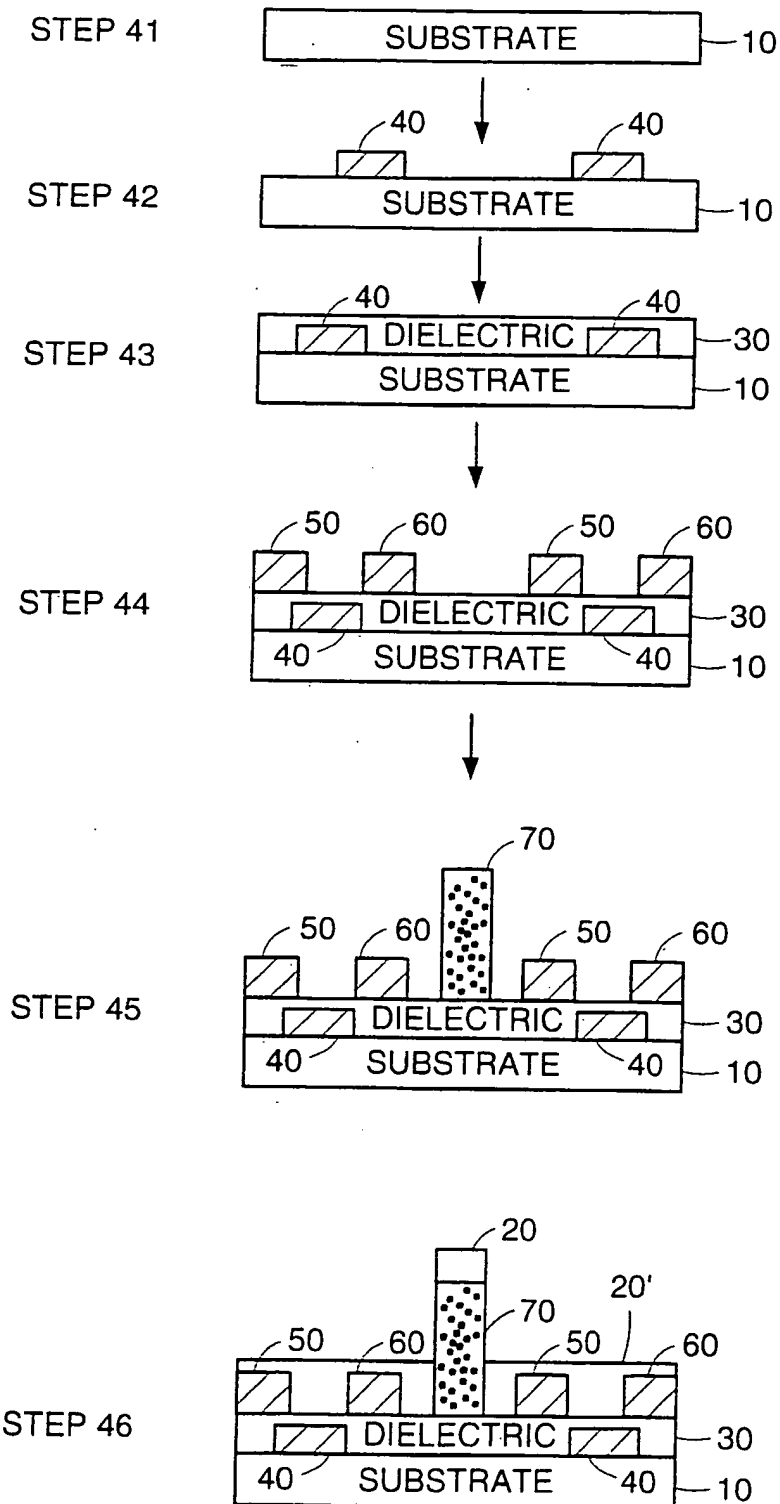


FIG. 4

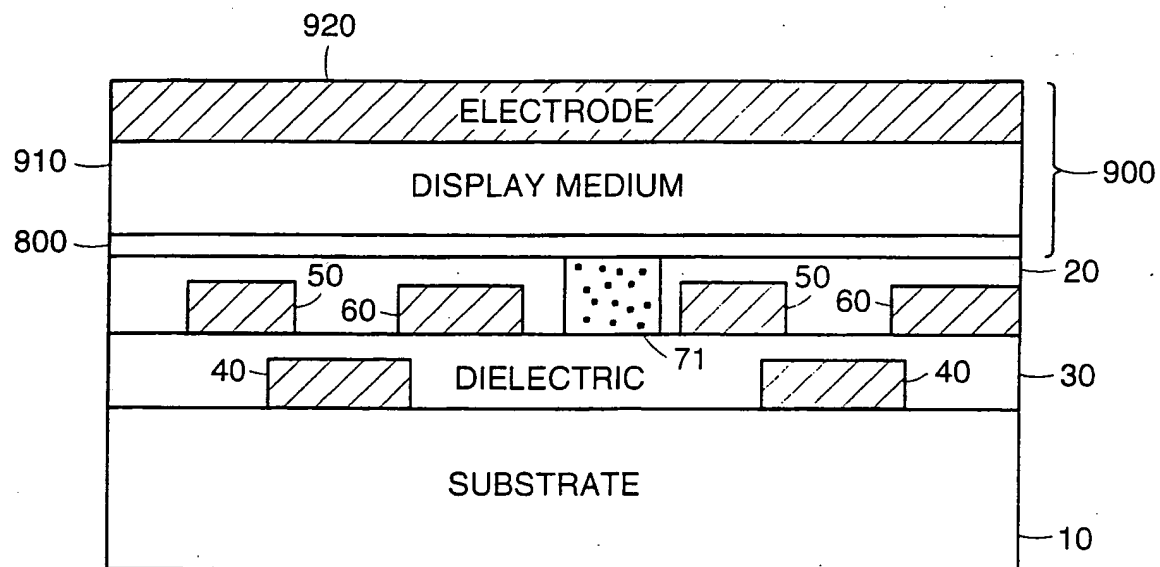


FIG. 5



5/5

TOP CONTACT PROCESS

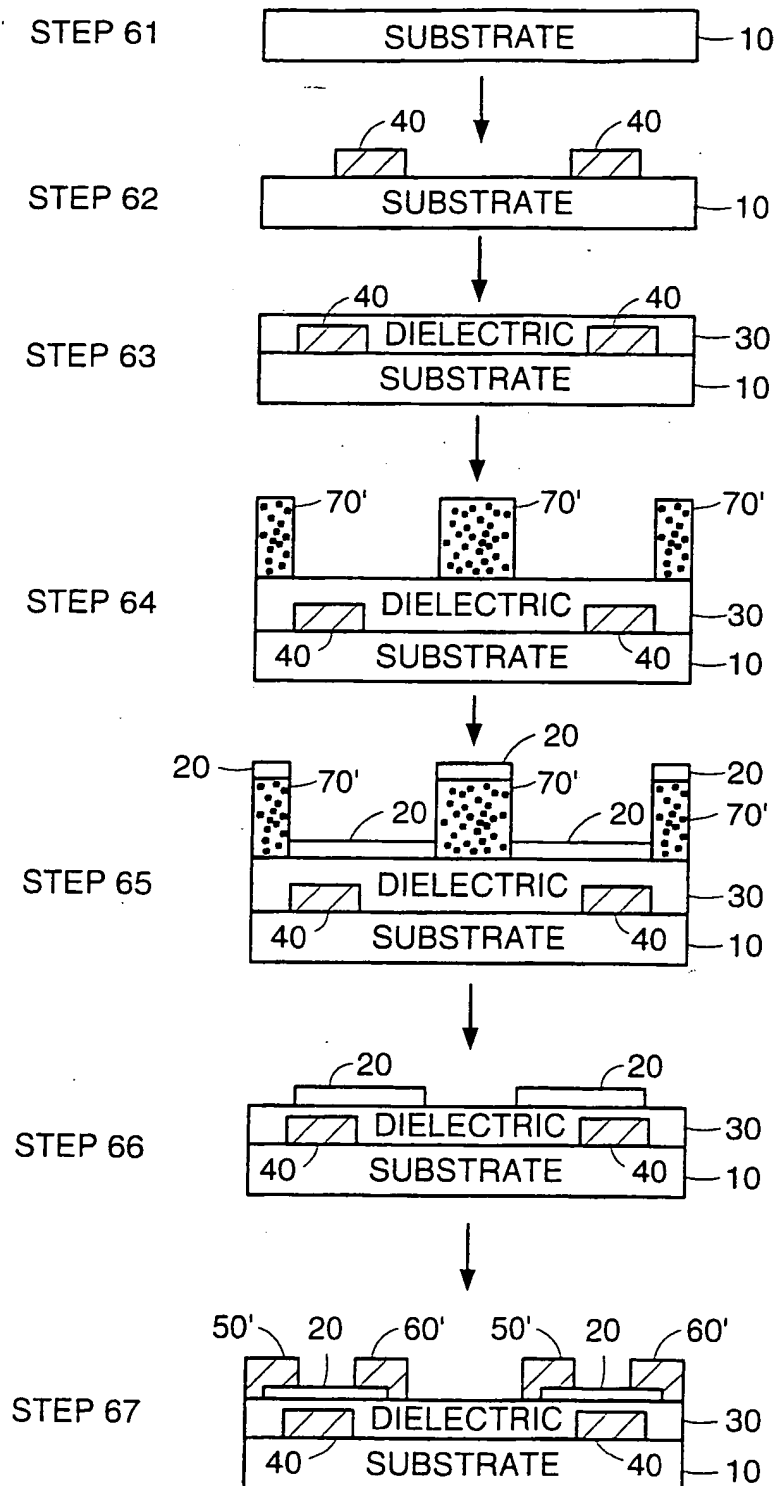


FIG. 6

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/24091

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01L51/40

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 930 641 A (SEIKO EPSON CORP) 21 July 1999 (1999-07-21) the whole document	1
A	GB 2 330 451 A (THIN FILM TECHNOLOGY) 21 April 1999 (1999-04-21) the whole document	1
A	WO 99 10939 A (KONINKL PHILIPS ELECTRONICS NV ;PHILIPS AB (SE)) 4 March 1999 (1999-03-04) the whole document	

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 November 2000

Date of mailing of the international search report

22/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

# INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 00/24091

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HEBNER T R ET AL: "INK-JET PRINTING OF            DOPED POLYMERS FOR ORGANIC LIGHT EMITTING            DEVICES"            APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE            OF PHYSICS. NEW YORK, US,            vol. 72, no. 5,            2 February 1998 (1998-02-02), pages            519-521, XP000737411            ISSN: 0003-6951            the whole document</p>	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**